Hydrazine—a Reducing Agent for Olefinic Compounds

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THE reaction of hydrazine with unsaturated carboxylic acids and other compounds has been studied in these laboratories for several years,[1–9] and it has been demonstrated that provided oxygen or some suitable oxidising agent is present and appropriate conditions (such as solvents, temperature and pH) are chosen, hydrazine can reduce olefinic (and also acetylenic) bonds in all the classes of compounds investigated. Of special interest were the observations that the hydrazine-oxygen system was able to reduce multiple double bonds in stages with apparently no *cis-trans* isomeric changes, or shifts in the positions of the double bonds, typical of the classical catalytic hydrogenation processes.[4,9] The reaction, a reduction in the presence of oxygen, appears to be of a very general application. Mechanistically it is of considerable interest. It promises to be of some practical importance, more especially as evidence has become available that an oxidation intermediate of the hydrazonium ion is the effective reducing agent.[6,7]

Our investigations arose out of work on the hydrogenation of phospholipids to obtain products of different degrees of saturation; the nickel-hydrogen technique was effective but difficulties were experienced in the subsequent removal of the metal from the surface active mixture.[10] A literature survey on methods of hydrogenation of unsaturated acids revealed a number of relatively isolated observations that hydrazine, well known as a reducing agent in inorganic chemistry,[11–14] could have some effect on olefinic bonds. Thus Hanus[15] and Falciola and Mannino[16] over half a century ago in the course of work on oleic hydrazide noted conversions to stearic derivative, and later studies were reported from Italy,[17] the Netherlands,[18] Czechoslovakia,[19–22] Germany,[23,24] Finland,[25] and Spain.[26] The general picture presented was that some fatty acids could be reduced by hydrazine, but that the reaction was slow and normally incomplete even after several days. Our initial experiments were designed to study the reaction between hydrazine and oleic acid in greater detail and in particular to see if the reaction rate could be increased by the correct choice of conditions; agitation of the mixture was found to be one controlling factor and it was noted that this effect might be due to an increased rate of decomposition of hydrazine, "perhaps because of increased exposure of the agitated solution to atmospheric oxygen."[1]

This paper reviews work that has been carried out to follow up this suggestion and to examine the mechanism of the reaction between hydrazine and olefinic acids and other unsaturated compounds in the light of the present knowledge of the intermediates formed from hydrazine by the action of oxidants.[12,27,28] Reference will also be made to recent reports from six other laboratories which reflect current interest in the hydrazine-unsaturated bonds reaction.

Reduction of Olefinic Carboxylic Acids

The necessity of oxygen or a suitable oxidising agent. In our earlier work[1] it was shown that oleic acid in ethanol solution was reduced fairly rapidly by hydrazine, provided the mixture was agitated in an open vessel, whereas with the unstirred solutions the rate of reduction was much slower. Thus with a hydrazine/oleic acid ratio of 5 : 1 over 8 hrs. at 50°c. the figures for percentage reduction were: with agitation 92%; without agitation 33%; whilst over 5 hrs. at 18°c. the figures were: 30% and 8%. Many similar experiments with different temperatures, concentrations of reactants and rates of agitation confirmed these results and revealed the importance of aeration.[6,7] The effect of oxygen was demonstrated under a wide variety of conditions. Thus rapid reduction of oleic acid was obtained using a stream of air or oxygen in place of a mechanical stirrer; on the other hand little or no reduction took place when a stream of nitrogen was used. In one series of experiments, stirring with oxygen gas gave 54% reduction in 1 hr.; with nitrogen 13% reduction was obtained; when the alcoholic solution of oleic acid was thoroughly saturated with nitrogen (all oxygen being displaced) before addition of hydrazine there was no reduction at all in 1 hr.

In open systems magnetic stirrers were found to give little or no reduction in contrast to mechanical stirrers, which broke the upper surface of the solution; in closed systems, with magnetic stirrers or shaking, the reduction was usually very slight and the results indicated that this was brought about through the action of oxygen initially present in the system.[7]

Various oxidising agents may be used in place of gaseous oxygen. Hydrogen peroxide, potassium iodate and potassium dichromate all promoted reduction in the hydrazine/carboxylic acid/alcohol system.[7]

Types of acids

Studies were carried out on a variety of olefinic acids (see Table I); with all those listed, 40–60% reduction was achieved over a 3 hr. period and it was concluded therefore that the reaction is of general application to mono- and poly-olefinic acids, short or long chain, provided there is no interference from side reactions with hydrazine.[7] Other acids which have recently been examined by different authors are listed in Table III.[32–37]

Absence of stable oxidation or nitrogen addition products

The mixed acids isolated after partial reduction of oleic acid were shown to consist of oleic and stearic acids only, by chemical and physical tests including spectroscopic examination.[1,7] These findings ruled out, therefore, the possibility of *stable* nitrogen or oxygen addition (acylic or cyclic) compounds being formed at the double bond. Similar results were obtained with other acids (see for example the detailed study of elaeostearic acid[4]). With a short chain compound such as acrylic acid there was some evidence that polymerisation or the formation of nitrogen-containing rings may take precedence over reduction.[7] In further experiments attempts were made to reduce by hydrazine (in the absence of oxygen) oxygen derivatives of oleic acid; such as epoxy-stearic acid and oleic acid hydroperoxide; but negative results were obtained.[7]

Evidence for the identity of the nitrogenous end product

The nitrogenous intermediate or end products from hydrazine reactions could conceivably include (apart from hydrazonium salts and hydrazides) the following: (I) molecular nitrogen, (II) ammonia, hydrazoic acid, or hydroxylamine, (III) nitrogen oxides or oxyacids, (IV) unstable hydro- or oxynitrogen derivatives in molecular or radical form.[12,27] The absence of nitrogen products in the isolated fatty acids has been noted above; further investigations demonstrated that the non-lipid part of the reaction mixture as isolated, contained no stable hydrazine degradation products, leading to the conclusion that such products would be found only in the gaseous phase. (It must be noted that these experiments did not rule out the possibility of *transitory* nitrogen-containing intermediates.) An extensive series of experiments (hydrazine, unsaturated acids in ethanol solution with aeration) failed to reveal any gaseous product except molecular nitrogen;[6,7] this is consistent with earlier studies on the oxidation of hydrazine under alkaline conditions.[27]

Effect of pH

The influence of pH on the reduction of carboxylic acids was examined using hydrazine hydrate with or without the additions of strong or weak acids or alkalis. It was found that, in ethanol solution, reduction took place only when the pH was on the alkaline side, with a $pH<7$ the results were always negative, and that the reaction was depressed with excess alkali, so that the maximum effect occurred in a relatively narrow pH range 8·5–9.[7]

Conductimetric experiments

Attempts were made to follow the hydrazine/carboxylic acid reaction by conductimetry, to see if information could be obtained on intermediate products. The records of different experiments showed that the conductance of hydrazine or fatty acid alone (in propyl alcohol solution) was low; on mixing, a rapid rise took place indicating the probable formation of $N_2H_5^+$ and $RCOO^1$ ions. During the course of the reduction (with oxygen present) the conductance rose slightly over an initial period and then began to fall. The conductances of artificially prepared reaction mixtures, corresponding to different stages of reduction, were lower than those of the true reaction mixtures. This suggested the possible formation of a conducting intermediate (not necessarily the reducing species).[7]

Effects of solvents

The reduction of unsaturated acids by hydrazine was demonstrated in several alcohols: methyl, ethyl, propyl, butyl, hexyl and octyl; and in methyl and ethyl cellosolves. Few differences were observed between these; the choice is largely one of convenience (for example in relation to the solubility of the fatty acid being investigated and the boiling point of the solvent).[7] There are certain advantages in using propanol, in that it simplifies studies of reaction rates through iodine value determinations; propanol (unlike ethanol) does not interfere with the reaction with the Wijs reagent, and so allows direct determinations to be made, subsequent to removal of hydrazine on an ion exchange column. When hexane or other non-polar solvents were used in place of alcohols, no reduction of oleic acid occurred even with vigorous stirring or aeration (hydrazine oleate is insoluble in hexane and was precipitated as a white mass). On the other hand, mixed solvents, such as hexane with ethanol or propanol can be used; but they tend to give somewhat lower reduction rates.[7]

Effects of temperature

The effects of temperature already noted[1] have been confirmed; in most experimental work it was convenient to work at 50°c., but the reaction can occur, although more slowly, at room temperature. Temperatures higher than 50°c. were normally avoided especially with compounds containing more than one olefinic bond because of the possible danger of polymerisation; moreover at the boiling point of the solvent the solubility of oxygen becomes zero and reduction is not possible (unless some oxidising agent is added).

Effects of catalysts

It is well known that various metallic ions, such as cupric ion, and other catalysts hasten the decomposition of hydrazine and that different end products can be obtained depending on the pH and other conditions (see Higginson's detailed review on the oxidation of hydrazine[27] and elsewhere[12]). It is also well established that the reduction of nitro compounds can be brought about by hydrazine in the presence of Raney Nickel.[38,39] At an early stage therefore the effect of Raney Nickel on the hydrazine/carboxylic acid system (with and without oxygen) was examined. In a typical experiment only 7% reduction of oleic acid was obtained in a 4 hr. period, by which time all the hydrazine had been destroyed. The results of different experiments suggested that the primary effect of Raney Nickel was to promote the degradation of hydrazine to nitrogen, hydrogen and ammonia, but that it made no contribution to the reduction reaction.[7]

In other experiments copper acetate was added (in concentrations 0·0005–0·002 moles) to the oleic acid/hydrazine/propyl alcohol/oxygen system; at 50°c. there was a slight increase in the percentage of acid reduced and a considerable increase in the amount of decomposed hydrazine, accompanied by the production of ammonia. Determination of copper contamination, in the ordinary reaction mixtures, showed it to be less than 1 p.p.m. The results suggested that cupric ion may promote the oxidation of hydrazine; there was no evidence that it had any effect on the reactivity with the double bond.[7]

Comparison of rates of reaction with *cis* and *trans* acids

More detailed studies (see Table I) have confirmed and extended the results already reported[2,4] that hydrazine can reduce both *cis* and *trans* forms of acids. There appears to be little difference in the rate of the reaction with isomers such as oleic (*cis*) and elaidic acid (*trans*) although the latter appears to be hydrogenated somewhat more slowly.[7]

Table I

Reduction of Olefinic Acids by Hydrazine-Oxygen System

Mono-Olefinic Acids	
β	(trans) Methyl acrylic (crotonic)[5]
β, β^{1}	Dimethyl acrylic[5]
α$_{1}$ β	Dimethyl acrylic (tiglic)[5]
Δ^{10}	Undecenoic[5]
Δ^{11}	(*trans*) Octadecenoic (vaccenic)[5]
Δ^{6}	(*cis*) Octadecenoic (petroselenic)[5]
Δ^{9}	(*cis*) Octadecenoic (oleic)[a,1]
Δ^{9}	(*trans*) (Octadecenoic (elaidic)[2]
	12-Hydroxy Δ^{9} octadecenoic (ricinoleic)[2]
Δ^{13}	(*cis*) Docosenoic (erucic)[8]
	(*trans*) Phenyl acrylic (cinnamic)[7]
	O-Hydroxy phenyl acrylic (*O*-coumaric)[7]
Di-Olefinic Acids	
2,4	Hexadienoic (Sorbic)[5]
9,12	Octadienoic (linoleic)[3]
Tri-Olefinic Acids	
9 *cis*, 12 *cis*, 15 *cis*	Octatrienoic (Linolenic)[9]
9 *cis*, 11 *trans*, 13 *trans*	Octatrienoic (Elaeostearic)[4]

a) Also with Hydrazine—KIO_3, $K_2Cr_2O_7$ and H_2O_2 systems.

Absence of isomeric changes during reduction

Experimental work on elaestearic acid[4] using U.V. and I.R. spectroscopy indicated that during hydrogenation by hydrazine there were no *cis-trans* isomeric changes or migration of double bonds. Direct evidence on the absence of the *cis-trans* transformations was obtained by infrared studies on linolenic acid[9] and on oleic acid[7] (and also on oleyl alcohol[7]). These findings have been extended by groups in Illinois[30] and Copenhagen[31] and their recent reports will be discussed later.

Table II

Reduction of Olefinic Alcohols, Sterols and Hydrocarbons by Hydrazine/Oxygen/Decoic Acid system

Alcohols and Esters	*Hydrocarbons*
2-Propen-1-ol (allyl)[7]	*A-cyclic*
2-Buten-1-ol (crotyl)[5]	2-Methyl-but-2-ene[d,7]
Δ^{9} (*cis*) Octadecen-1-ol (oleyl)[a,5]	Oct-1-ene[5]
Δ^{13} (*cis*) Docosen-1-ol (erucyl)[5]	Oct-2-ene[5]
Allyl acetate[7]	Dec-1-ene[5]
Sterols and Sterol Esters [b,c]	Dodec-1-ene[5]
Cholesterol[7]	Octadec-1-ene[5]
Δ^{7} Dehydrocholesterol[7]	Stilbene[7]
Lanosterol[7]	*Alicyclic*
Stigmasteryl acetate[7]	Cyclohexene[5]

(*a*) Also by hydrazine/hydrogen peroxide system, and hydrazine/decoic acid/potassium iodate or dichromate system.
(*b*) In a mixture of alcohol and chloroform.
(*c*) Also use of potassium iodate at reflux conditions.
(*d*) At room temperature.

Reduction of Other Olefinic Compounds

Preliminary experiments on oleyl alcohol.[5,7] When oleyl alcohol was treated with hydrazine under the conditions successfully used for oleic acid no reduction occurred and attempts were therefore made to find the reason for the difference between the reaction of the acid and the alcohol. The possible formation of the hydrazonium ion in the presence of the organic acid appeared to be a significant feature. It was demonstrated that the addition of a weak saturated acid to the oleyl alcohol/hydrazine mixture brought about reduction. Among the acids used were acetic, butyric and decoic (capric); by such additions the rate of hydrogenation of oleyl alcohol approximated to that found for oleic acid. In subsequent experiments decoic acid was used as the standard additive. Conductimetric studies showed that in propanol solution a significant conductance could be attributed to the ionisation of the hydrazonium salt of decoic acid. When hydrogen peroxide was used in place of oxygen reduction occurred without the addition of an acid such as decoic, presumably because the peroxide itself has weakly acidic properties.

Extension to other olefins[5,7]

The investigation was extended (see Table II) to other olefinic compounds including hydrocarbons, alcohols and sterols; in all cases the hydrazine-oxygen system alone gave negative results, but reduction was successfully brought about through the addition of decoic acid. Various modifications of technique were necessary to deal with different compounds depending on their volatility or solubility. Thus with 2-methyl 2 butene, it was necessary to work at room temperature and consequently the rate of reduction was slower (22% in 24 hrs.). With sterols it was found advantageous to use methyl cellosolve as a solvent and to heat the mixture under reflux on a water bath with KIO_3 as a source of oxygen but mixed solvents (chloroform–ethanol) at 50°c. with aeration have also been used successfully. Many of the investigations already noted in relation to carboxylic acids were repeated with oleyl alcohol and other olefins and the results were in every case confirmed and extended. Thus (providing decoic acid was present) reduction took place with both *cis* and *trans* forms of olefins; moreover the reagents did not produce *cis-trans* or positional isomeric changes.

The discovery that the hydrazine oxygen reducing system applied to olefinic compounds generally clearly opens up a wide field of investigation. This is illustrated by recent communications covering the reduction of a variety of compounds including (see Table III) the reduction of allyl sulphide to propyl sulphide, not achieved previously by any other means.[37]

Stoichiometric Relationships and Kinetics

Hydrazine olefin reactant ratios: Early experiments[1] showed the necessity of an excess of hydrazine in relation to oleic acid. Thus in a typical series (using ethanol as a solvent at 50°c.) increasing molecular ratios hydrazine/oleic acid were used at 50°C. After 1 hr. with the 1 : 1 ratio the reduction was very slight (6%); the 2 : 1 ratio gave a much higher figure (23%). Other work confirmed the importance of a minimum ratio 2 : 1 in the reduction of fatty acids and other compounds (such as oleyl alcohol) containing one double bond. In general there was little point in using a ratio greater than 2 : 1; however, when oxidants such as hydrogen peroxide were used in place of oxygen, a greater excess of hydrazine was required.

The earlier experiments[3,4] showed that with di- and poly-olefinic acids higher initial ratios of hydrazine/acid were necessary; thus with elaeostearic a 2 : 1 ratio gave only 15% reduction in 8 hrs., cf. 74% with a 6 : 1 ratio. Later work confirmed that the initial quantities of hydrazine should be calculated on the number of double bonds so that for di-enoic compounds the minimum desirable ratio was 4 : 1 and for tri-enoic compounds 6 : 1.

Relationship between hydrazine utilised and olefin reduced[7]

Several series of investigations were carried out with measurements of the rate of reduction and of hydrazine utilised under different experimental conditions including (I) different initial ratios of hydrazine: olefin, (II) different rates of aeration, or (III) use of oxidising agents instead of oxygen.

When the rate of stirring was adjusted to produce mild aeration, it was shown (with oleic acid–ethanol at 50°C.) that in spite of different initial ratios of hydrazine/acid and the variations in the amount of reduction achieved (40–85%) over periods 1–8 hrs., the ratio reacted hydrazine/reacted oleic acid was usually about 2 : 1. In further experiments, a stream of oxygen or air was used in place of a mechanical stirrer and conditions were standardised so that the rate of oxygenation could be measured. It became evident that the rate of hydrazine degradation increased with increasing oxygen uptake; at low concentration of oxygen, the ratio of reacted hydrazine/reacted oleic acid was approximately 2 : 1; with excess oxygen the ratio rose indicating that oxygen was playing a direct part in the destruction of hydrazine.

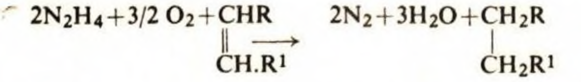
The results of many different experiments with oleic acid and other compounds under a variety of conditions suggested that two distinct processes took place.

(a) The action of hydrazine in the presence of oxygen in reducing the olefin to give as end products nitrogen, water and the saturated compound; the molecular ratio of hydrazine : oleic acid being 2 : 1.

Table III

Reduction of olefinic bonds by Hydrazine—Oxygen or Equivalent Systems

	Hydrazine/ Oxygen System	*Hydrazine/H_2O_2*	*Hydrazine/ $K_3(Fe(CN)_6)$*	*Potassium azodiformate*	*Benzene sulphonyl hydrazide*	*p-toluene sulphonyl hydrazide*
Acids:	Maleic[32]	Fumaric[32] *cis*-Δ4-cyclohexene, 1,2-dicarboxylic[32] gibberellic[32] exo-Δ5-norbornene-2-carboxylic[32] dimethylmaleic[33]	Maleic[34] Fumaric[34] 10-undecenoic[34] (also with HgO) cinnamic[34]	Maleic[33] Fumaric[33] 10-undecenoic[34] Oleic[35] Elaidic[35]	10-undecenoic[34]	Oleic[36] Elaidic[36]
Hydrocarbons:	Stilbene[32]	cyclopentadiene[32]		Cyclohexene[35] Stilbene[35]	Dicyclopentene and pentadiene[34]	Cyclohexene[36]
Alcohols:		*Cis* and *trans* 2-Butene 1,4 diols[33]		Allyl[35]		Allyl[36]
Sterols:	Cholesterol[32]					
Others:				Quinine[35]		Allyl sulphide[37]



$$2N_2H_4+3/2\,O_2+\underset{\text{CH.R}^1}{\overset{\text{CHR}}{\|}} \longrightarrow 2N_2+3H_2O+\underset{\text{CH}_2\text{R}^1}{\overset{\text{CH}_2\text{R}}{|}}$$

(b) The oxidation of hydrazine in alkaline solution by oxygen to give nitrogen and water.

$$N_2H_4+O_2 \longrightarrow N_2+2H_2O$$

It was recognised that both (a) and (b) could take place in various stages and that the initial stage might be common to both, i.e. oxidation to produce a common intermediate which can either react with oleic acid as in (a) or be oxidised further as in (b). Moreover as already noted the initial reactions may proceed through hydrazonium ion $N_2H_5^+$.[6] These and allied mechanisms will be discussed later.

Our results showed that the relative importance of reactions (a) and (b) varied with several factors, e.g. with the oxygen availability and pH; with high concentration of oxygen reaction (b) became predominant and reaction (a) was suppressed. Under one set of experimental conditions the maximum rate of reduction of oleic acid, in the initial period of 15 minutes, was obtained with rates of passage of oxygen 600 ml./minute; subsequently the rate of reduction of oleic acid slowed down, but the destruction of hydrazine by oxygen continued with the liberation of nitrogen.

Closed system experiments with measurements of oxygen utilised and nitrogen liberated[7]

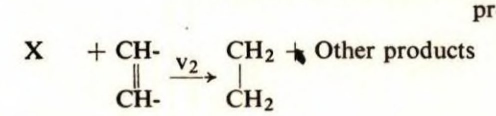
Experiments were carried out in which mixtures of oleic acid/hydrazine/alcohol were placed in 250 ml. narrow necked flasks fitted with outlet tubes and taps; the air in solution and in the flask was replaced by a known amount of oxygen and the mixtures were shaken for 3–4 hrs., after which time the oxygen and nitrogen were measured together with the changes in hydrazine and oleic acid concentrations. The results were consistent with the two equations proposed (a) and (b) and indicated that as in (a) the ratios of hydrazine : oxygen : olefin were 2 : 3/2 : 1.

Kinetic studies[7]

Kinetic studies were carried out on the reduction of olefinic compounds; for various reasons (including the possibility of controlled pH by the addition of decoic acid instead of having an acid as one of the major reactants) the oleyl alcohol system is more suitable than the oleic acid system for some investigations. The results obtained suggest that the processes for the reduction of olefinic bonds by the hydrazine-oxygen system can be summarised:

I $2N_2H_5^+ + O_2 \xrightarrow{v_1}$ Reactive Intermediate X + Other products

II



$$X + \underset{\text{CH-}}{\overset{\text{CH-}}{\|}} \xrightarrow{v_2} \underset{\text{CH}_2}{\overset{\text{CH}_2}{|}} + \text{Other products}$$

III $X + O_2 \xrightarrow{v_3}$ products

The reaction rates are as follows:

$$v_1 = k_1\,[O_2]\,[N_2H_5^+]^M$$
$$v_2 = k_2\,[\text{-CH=CH-}]\,[X]$$
$$v_3 = k_3\,[O_2]$$

There is a difficulty in regard to I because of the problem of determining the concentration of $N_2H_5^+$, but the orders of II, III, and constant k_3 have been determined; the absolute value of k_2 cannot yet be calculated, although comparisons can be made for different olefins. Our results show that k_3 varies with pH being 0·13–0·16 at pH 8·5 and rising to 0·4 at pH 10 (propanol 50°c.).

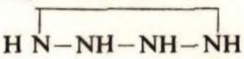
The kinetic experiments provided us with a direct proof that an oxidation product of hydrazine is the effective reducing agent. We have found that the decomposition of hydrazine depends only on the concentration of hydrazonium ion and oxygen, and is only influenced by the presence of the olefinic compound in so far as less oxygen is required for complete decomposition.

Evidence from oxidation studies

A literature review suggested that the most likely intermediate is one of the unstable hydronitrogens or their radicals postulated by earlier workers such as *Thiele*[40] *and Raschig*[41] *and discussed in detail by* Kirk and Browne,[28] Higginson,[27] and Audrieth and Ogg,[12] who have studied or reviewed the oxidation of hydrazine under different conditions. Higginson on the basis of his very detailed survey on oxidation believes "it is now clear that various short-lived hydronitrogens either free radicals or molecules, are formed in the oxidation of hydrazine. Evidence for their existence in aqueous systems arises in the interpretation of recent kinetic and tracer work."

The use of the hydrazine-methanol-hydrogen peroxide system as a rocket fuel stimulated fundamental work on oxidation mechanisms and recent as well as older investigations have emphasised that, although the possible end products isolated from oxidations are normally simple (nitrogen, ammonia, hydrazoic acid and water), great variations in the relative quantities of these products (and presumably therefore in the reaction mechanisms) occur under different experimental conditions; they depend in particular on the type and concentration of the oxidising agent, temperature, pH and the presence of polyvalent metallic or complex ions.

The work of Kirk and Browne[28] is important in the present context because they distinguished for the first time between 1- and 2-equivalent oxidative changes; and provided evidence that different primary products (and therefore different end products) were obtained from hydrazine with the two systems. Thus they believed that 1-equivalent oxidation gave the hydrazyl radical (N_2H_3), whereas 2-equivalent oxidation gave diazen (diimide) (N_2H_2). Various modifications of the Kirk and Browne reaction mechanism have become necessary as a result of tracer and other studies.[42,43] It has been noted [12,27] that relatively few quantitative studies have so far been carried out on the oxidation of hydrazine under alkaline conditions, and that errors have probably occurred in published work because of the lack of appreciation of the action of atmospheric oxygen on alkaline solutions, although this was first observed at least 30 years ago.[44] Recent studies have emphasised three characteristics of hydrazine oxidations at high pH values: (a) the catalytic effect of polyvalent metal ions, (b) the low or negligible yields of ammonia (in contrast to nitrogen) and (c) the formation under certain conditions of hydrogen peroxide.[12] Among the many oxidation intermediates proposed are the hydrazyl radical (N_2H_3); diazen or diimide (N_2H_2) and dimers such as tetrazan (N_4H_6) and tetrazen (N_4H_4), and triazen (N_3H_3). Various formulae have been suggested for each of these including:

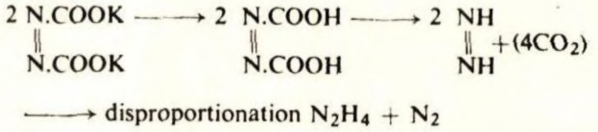
Diazen:	Linear symmetrical	$HN{=}NH$
	Linear unsymmetrical	$H_2N^{\oplus}{=}N^{\ominus}$
Tetrazen:	Linear symmetrical	$H_2N{-}N{=}N{-}NH_2$
	Linear unsymmetrical	$H_2N{-}NH{-}N{=}NH$
	Cyclic	

Diazen was first postulated by Thiele[40] and Raschig[41] who attempted unsuccessfully to prepare it by classical methods and, since the work of Kirk and Browne, it has been regarded as one of the keys to hydrazine oxidation. Suggestions have been made of a linear paramagnetic form and a bent planar diamagnetic form.[45] Recent studies have provided evidence, from mass spectroscopy, that diazen is among the products obtained by an electrodeless discharge through hydrazine and that it may exist in the solid state at −195°C.[47] In the various schemes proposed for the oxidation of hydrazine it is assumed that diazen can function either as a hydrogen donor or hydrogen acceptor and can react with oxygen to give nitrogen and water or undergo disproportionation ($2N_2H_2 \longrightarrow N_2H_4 + H_2$).[27] The evidence for the existence of tetrazen and tetrazan is discussed by Higginson.[27] Recent investigations have indicated that tetrazan is formed by passing hydrazine vapour through a furnace at 850°C. and may be obtained as a yellow diamagnetic solid by freezing the products at −195°C.[48] It can therefore be concluded from the above oxidation and related studies (a) that one or more intermediates are formed by oxidation, depending on the conditions, (b) that these intermediates can undergo various reactions (and inter-reactions) to give the end products of oxidation, and (c) that they can be expected to react with other compounds (such as olefins) added to the hydrazine-oxygen system.

Reduction of olefins by systems related to hydrazine

In the classical (unsuccessful) attempts to prepare diazen two reactions received special attention; the decomposition of (a) potassium azodiformate and (b) benzene (or p-toluene) sulphonyl hydrazide.

Thiele suggested that hydrolysis of potassium azodiformate proceeds according to the following scheme:



$$2\,\begin{matrix}N.COOK\\ \|\\ N.COOK\end{matrix} \longrightarrow 2\,\begin{matrix}N.COOH\\ \|\\ N.COOH\end{matrix} \longrightarrow 2\,\begin{matrix}NH\\ \|\\ NH\end{matrix} + (4CO_2)$$

$$\longrightarrow \text{disproportionation } N_2H_4 + N_2$$

Other authors[32,34,35,49] have also assumed a similar mechanism although it has been pointed out that, as an alternative to disproportionation, hydrazine could be formed by reduction of the azo-acid (by diazen) to the hydrazo acid followed by decarboxylation.[34] The decomposition of aromatic sulphonyl hydrazides according to Raschig[41] proceeded as follows:

$$C_6H_5SO_2NHNH_2 \xrightarrow{\text{alkali}} \underset{\text{phenyl sulphinate}}{C_6H_5SO_2Na} + N_2H_2 + H_2O$$

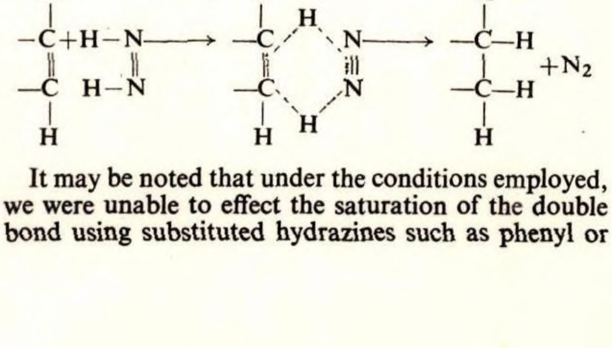
$$4C_6H_5SO_2NHNH_2 \longrightarrow C_6H_5SO_2SC_6H_5 + C_6H_5SSC_6H_5 + 4N_2 + 6\,H_2O$$

In recent months six short reports have appeared from three groups of workers, who have demonstrated that under appropriate conditions both azodicarboxylic acid and benzene (or p-toluene) sulphonyl hydrazide can reduce a variety of olefins (see Table III). This work strongly suggests that diazen is the effective intermediate in hydrazine-oxygen reducing system.

Further evidence for Diazen as the active intermediate in the reduction of olefins

In addition to studies of the reactions (a) and (b) the recent papers provide information of the wide range of olefinic compounds (see Table III) that can be reduced by hydrazine provided suitable conditions are chosen. There is complete agreement that oxygen or an oxidising agent is necessary. The Munich group[34] used oxidants such as potassium ferricyanide and mercuric oxide as well as air and using Δ^{10} undecenoic acid were able to work in an aqueous alkaline system. The Harvard workers[32,33] studied the reducing action in the presence of air (or oxygen) and also with hydrogen peroxide and other reagents. Both groups noted that the oxidants, found to be effective, were those (two-equivalent) which are believed (on the basis of oxidation studies) to give diazen; they therefore proposed the following mechanism:

(I) Hydrazine ⟶ Diazen
(II) Diazen + olefin ⟶ Unstable cyclic compound (U) by addition to double bond.
(III) Decomposition of U ⟶ Reduced olefin + N_2



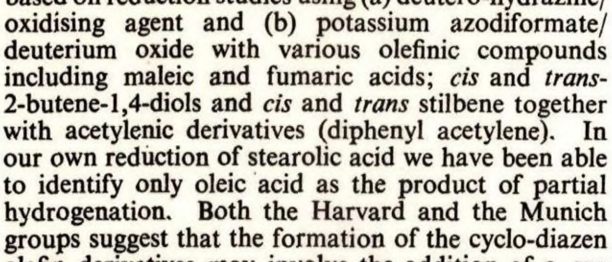
It may be noted that under the conditions employed, we were unable to effect the saturation of the double bond using substituted hydrazines such as phenyl or hydroxyethyl hydrazine. The substituted diazens, formed as intermediate products of oxidation, could not be expected to react with double bonds according to the above mechanism.

The Harvard group noted the effect of copper ion in catalysing both the hydrazine/oxygen and hydrazine/hydrogen peroxide reducing systems. The effect of this ion may be more pronounced in their experiments at 25°c than in those discussed earlier and normally carried out at 50°c.[7] They observed also the reduction of azobenzene to hydrazobenzene by hydrazine, a reaction which was useful for test purposes because of the colour change and, in agreement with the Munich group, found that acetylene derivatives could be reduced.

Stereochemical and allied studies[32,33,7]

The Munich workers examined the reduction of phenyl propiolic acid and found that the cinnamic acid produced was primarily *cis;* the Harvard workers also concluded that the addition "was quite generally *cis*, a finding in accord with the behaviour expected of a hydrogenating agent which derives its reactivity from formation of a very stable molecule after the transfer of a pair of hydrogens." Their evidence was based on reduction studies using (a) deutero-hydrazine/oxidising agent and (b) potassium azodiformate/deuterium oxide with various olefinic compounds including maleic and fumaric acids; *cis* and *trans*-2-butene-1,4-diols and *cis* and *trans* stilbene together with acetylenic derivatives (diphenyl acetylene). In our own reduction of stearolic acid we have been able to identify only oleic acid as the product of partial hydrogenation. Both the Harvard and the Munich groups suggest that the formation of the cyclo-diazen olefin derivatives may involve the addition of a *syn* form of diazen and "that this implies either that this isomer is generated directly or that the *syn* and *anti* forms are in rapid equilibrium."

The stoichiometric and kinetic studies, reported earlier in this review show that two molecules of hydrazine produce only one effective reductant molecule which, in turn, reacts with one double bond. It is, therefore, possible that an equivalent mixture of *syn* and *anti* diazen is being formed, of which only the *syn* form is capable of reacting with the double bond. We suggest that the hydrazonium ion is oxidised initially to a protonated form of diazen which then loses its proton giving rise to a mixture of the two isomers.



The fact that the proton is lost before the reduction step is suggested indirectly by the conductimetric measurements. The conductivity change appears to be independent of the presence of double bonds, indicating that the reduction step is non-ionic. At this stage we are not able to rule out the possibility of a mixture of symmetrical and unsymmetrical diazens or other intermediates being involved.

Practical Applications

Prevention of reduction by exclusion of oxygen: Hydrazine is used for a variety of purposes in organic chemistry and classical reactions include (in addition to hydrazide formation) condensations with carbonyl and other groups. It is evident that if an olefinic or acetylenic compound is being used in such a reaction, then reduction of the multiple bond may take place, unless oxygen is excluded from the system.

The reduction of unsaturated acids during hydrazide formation has already been discussed and Hunig and Eckardt[34] have noted the reduction of the olefinic bond in unsaturated ketoacids during the Wolff-Kishner reaction. Malkin[29] in his synthesis of dioleyl cephalins followed the Baer technique of removing, in the final stage, a phthalyl group by hydrazine; he found the product to be contaminated by the distearoyl compound but, following discussions with one of the present authors (F.A.), was able to complete the synthesis successfully in an atmosphere of nitrogen. The variable results noted by Cross[50] in his work on gibberellic acid were probably due to insufficient oxygen. On the basis of current knowledge, it would appear desirable to re-examine some of the older work involving hydrazine and unsaturated substances to see how far reduction products were formed. In some cases, e.g. in hydrazide formation,[51] the reflux conditions used may have minimised the possibility of reduction.

Model reduction system

The observations that hydrazine can reduce fatty acids without *cis-trans* or positional isomeric changes, suggest that the hydrazine reaction may provide an important new technique in lipid chemistry for the examination of unsaturated and particularly polyunsaturated acids. The study of such acids is of importance, at the present time, because of their occurrence in foodstuffs and their role in lipid metabolism and also because of their uses as sources of polymers. The earlier work on elaeostearic acid[4] enabled comparisons to be made with catalytic hydrogenation techniques and Dutton and his colleagues in Illinois have made a similar study of linolenic acid.[30] This *cis-cis-cis* compound gives, on catalytic (partial) hydrogenation, a complex mixture of *cis* and *trans* compounds including nine monoenes and four dienes, whereas reduction by hydrazine gave only the components to be expected on the basis of hydrogenation without isomerisation. The Illinois authors have pointed out that hydrazine reduction may be expected to provide reference compounds for comparison with those obtained by other reduction methods.

Our work indicates that the reduction of non-acidic compounds, such as oleyl alcohol, is also characterised by the absence of isomeric changes and if this should be shown to be true of all hydrazine reductions then the technique may be of value in the study of the structure and degradation products of different types of unsaturated compounds (such as sterols containing more than one olefinic bond, polyene pigments and other natural as well as synthetic polymers).

Preparations by selective partial reductions

The elaeostearic acid investigations[4] indicated some selectivity in hydrogenation of a poly-unsaturated compound, and Schilling of Copenhagen[31] has recently demonstrated that the hydrazine reduction technique is of use in the preparation of certain unsaturated acids. There are older observations indicating that selective reductions may occur with non-carboxylic compounds; for example with porphyrins and chlorins, the transformation of vinyl to ethyl groups.[23,24] In such reductions the hydrazine/oxygen system may have special advantages when it is desirable to avoid the use of catalysts such as nickel and to work in a variety of solvents under different temperature conditions. It also seems likely, on the available evidence, that this reducing system may be of use in relation to various types of polymers.

Analogies with biochemical reactions

Among the interesting features of the hydrazine reaction are: (I) it is unusual because it involves a reduction in the presence of oxygen (or an oxidant), (II) it takes place in two or more stages, the initial oxidation of hydrazine followed by the reduction of the olefin, (III) it involves the formation of a reductant as an unstable intermediate, (IV) it proceeds under mild temperature conditions, and (V) over a narrow pH range, (VI) the reduction has been shown to have a high degree of stereospecificity and (VII) under certain conditions metallic ions may function as catalysts. Because of the above considerations it is tempting to seek analogies in those biochemical redox systems characterised by a chain of linked reactions with transitory intermediates functioning in a limited pH range.

The Wisconsin workers[36] have pointed out that there are few analogies (in inorganic chemistry) for reactions involving short-lived substances of the diazen (or related) types; and that the hydrazine reaction points to the possibility of finding other inorganic short-lived intermediates, which can bring about different types of organic reactions, in the same way as organic entities such as carbenes have been successfully used in preparative work. This is one of the new fields that may be opened up following the hydrazine investigations and the studies of what has been described as a "unique hydrogenation."[32]

Acknowledgment

The authors thank the Nuffield Foundation for support of this work.

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